Aromatic Hydroxylation. Part 7.[1] Oxidation of Some Benzenoid Compounds by Iron Compounds and Hydrogen Peroxide with the Aromatic Compound acting as Substrate and Solvent

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The oxidation of some monocyclic aromatic compounds, in the presence of tris(acetylacetonato)iron(III), with hydrogen peroxide has been investigated. The evidence presented suggests that the attacking species is the hydroxyl radical and that the mechanisms of these reactions, in which the aromatic compound serves as substrate and solvent, are very similar to those of the hydroxyl radical in aqueous solution. Thus benzene gives phenol and biphenyl, anisole gives phenol and methoxyphenols, and toluene gives a mixture of products from ring and side-chain oxidation. The oxidations can also be carried out using several other benzene-soluble iron compounds although benzene containing hexacyanoferrate-(II) and -(III), solubilised with Adogen 464, is stable to oxidation

THE hydroxylation of aromatic compounds by the hydroxyl radical in an aqueous medium has been the subject of extensive studies. Thus the hydroxyl radical, generated by the reaction of iron(II) salts with hydrogen peroxide (Fenton's reagent),[2] by radiolysis of water with *X*-rays,[3] γ-rays,[4] and pulsed electron beams,[5] and by the u.v. photolysis of hydrogen peroxide [2b,6] has been used to oxidise a wide range of monocyclic [2b,4c–e,5c–e] and polycyclic aromatic compounds.[4a,7] From structural and kinetic studies on the transient intermediates in these oxidations [5,8] and from the distribution of products [2b,4c–f,7c] the mechanisms of these reactions of the hydroxyl radical are well understood and have been collated by Walling and Johnson.[9] Recently we have extended this work to include the hydroxylation of aromatic compounds by Fenton's reagent in dipolar aprotic and aqueous dipolar aprotic solvents.[10]

In this paper we report our results on the hydroxylation of benzene and some benzene derivatives by Fenton's reagent with the aromatic compound as the substrate and solvent. It was hoped that by utilising the aromatic compounds thus, the large excess of substrate would maximise the conversion of hydrogen peroxide to phenols and minimise the further oxidation of the products.

RESULTS

Oxidation of Benzene with $Fe^{III}(acac)_3$† *and Hydrogen Peroxide under Air or Nitrogen.*—When hydrogen peroxide was added to a benzene solution of $Fe^{III}(acac)_3$ in air, phenol, in low yield, was the sole product from the benzene detectable by g.l.c. analysis. Repeated additions of hydrogen peroxide increased the overall yield although the conversion of benzene to phenol per portion of hydrogen peroxide remained constant at *ca.* 4% (based on hydrogen peroxide, for each of four additions). The product formation was monitored and measured by g.l.c. analysis and typically the reactions were complete within 1 h of the addition of the hydrogen peroxide. Analysis 24 h after the addition of the hydrogen peroxide showed no diminution of the yield of phenol. When the reaction was carried out under nitrogen, phenol and biphenyl were formed in 4 and 0.2—0.4% yield, respectively, per portion of hydrogen peroxide. The reaction flasks at the end of the reactions carried out in air or under nitrogen contained a small amount of a dark deposit. The dark deposit from a large-scale oxidation was dried and shown to contain 10.1% iron.

The reaction in air was repeated with a ten- and a hundred-fold decrease in the concentration of the $Fe^{III}(acac)_3$. In the former the yield of phenol was reduced to 0.5—0.7% per portion of hydrogen peroxide and in the latter only a trace of phenol was detected. In both experiments the addition of hydrogen peroxide resulted in a bleaching of the colour of the solutions, with the latter becoming colourless after the first addition of hydrogen peroxide. Blank experiments showed that in the absence of $Fe^{III}(acac)_3$ or of hydrogen peroxide no oxidation of benzene occurred. Further, the reaction of a synthetic mixture of phenol in benzene, in the concentration present at the end of a typical oxidation, with $Fe^{III}(acac)_3$ and hydrogen peroxide showed no measurable loss of phenol by further oxidation.

Oxidation of Benzene with Hydrogen Peroxide and a Selection of Iron Compounds.—The oxidation of benzene by hydrogen peroxide was repeated with the $Fe^{III}(acac)_3$ solution replaced by solutions containing an equivalent amount of $Fe^{II}(acac)_2$, Fe^{III}TPPCl, ferrocene, pentacarbonyliron, or iron(III) chloride in air and under nitrogen (Table 1). The reactions with FeTPPCl and ferrocene took longer to come to completion and only those with $Fe^{II}(acac)_2$ and Fe^{III}TPPCl gave similar yields to that from $Fe^{III}(acac)_3$. The other iron compounds gave low yields or no detectable oxidation products. Biphenyl was only detected in the oxidation with $Fe^{II}(acac)_2$ under nitrogen.

Oxidation of Benzene with $Fe^{III}(acac)_3$ *and Hydrogen Peroxide under Heterogeneous and Homogeneous Conditions.*—(a) The oxidation of benzene with $Fe^{III}(acac)_3$ and hydrogen peroxide under air or nitrogen was repeated replacing the glass reaction vessel with a polythene container. The yields of phenol and biphenyl respectively were unaffected by this change.

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† The following abbreviations are used in this paper: $Fe^{III}(acac)_3$, tris(acetylacetonato)iron(III); $Fe^{II}(acac)_2$, bis(acetylacetonato)iron(II); and Fe^{III}TPPCl, tetraphenylporphinatoiron(III) chloride.

TABLE 1

Yield of phenol and biphenyl from the oxidation of benzene by hydrogen peroxide and iron compounds in air or nitrogen

Iron compound	Reaction conditions	Reaction time (h)	% Yields * Phenol	% Yields * Biphenyl
$Fe^{III}(acac)_3$	Air	1	4.4	0
	N_2	1	4.2	0.3
$Fe^{II}(acac)_2$	Air	1	3.9	0
	N_2	1	4.1	0.2
$Fe^{III}TPPCl$	N_2	6	6.0	0
Ferrocene	N_2	6	1.9	0
$Fe(CO)_5$	N_2	1	1.2	0
$FeCl_3$	N_2		0	0

* Product yields determined by g.l.c. analysis and based on H_2O_2.

(b) When the $Fe^{III}(acac)_3$ was dissolved in a portion of a saturated solution of hydrogen peroxide in benzene, phenol was obtained in 3.1% yield.

(c) The yields of phenol and biphenyl from the oxidation of benzene with hydrogen peroxide in benzene–acetonitrile mixtures containing $Fe^{III}(acac)_3$ under nitrogen were measured (Table 2). The data show that the yields of phenol and biphenyl are highest when the proportion of the benzene in the solvent is greatest and that there is no marked alteration in the product distribution when the reaction conditions are changed from a heterogeneous system in pure benzene to a homogeneous one in mixed benzene–acetonitrile.

TABLE 2

Yield of phenol and biphenyl from the oxidation of benzene with $Fe^{III}(acac)_3$ and hydrogen peroxide in benzene–acetonitrile mixtures

Product yield * (%)	Solvent composition (benzene % v/v) 100	90	80	70	60	50	40	30	20	10
Phenol	3.6	3.5	2.3	2.2	1.9	2.0	1.5	0.9	0.8	0.5
Biphenyl	0.3	0.3	0.3	0.3	0.3	0.2	0.2	0.2	0.2	0.1

* Product yields determined by g.l.c. and based on H_2O_2.

Attempted Oxidation of Benzene with $Fe^{III}(acac)_3$ *and* $Fe^{III}TPPCl$ *and a Selection of Oxidants in Place of Hydrogen Peroxide.*—No oxidation products from benzene were detected when benzene solutions of $Fe^{III}(acac)_3$ in air were mixed with any of the following: iodosylbenzene, t-butyl hydroperoxide, and cumene hydroperoxide, or when a benzene solution of $Fe^{III}TPPCl$ was treated with iodosylbenzene.

Oxidation of Toluene and Anisole with $Fe^{III}(acac)_3$ *and Hydrogen Peroxide.*—The addition of hydrogen peroxide to toluene containing $Fe^{III}(acac)_3$ under nitrogen gave benzaldehyde, benzyl alcohol, bibenzyl (trace), and all three cresol isomers (Table 3). The corresponding oxidation of anisole in air gave phenol and the methoxyphenols (Table 3). The overall yields from these oxidations of benzene derivatives are approximately the same as those from the oxidation of benzene.

NIH Shift of Deuterium during the 4-Hydroxylation of 4-Deuterioanisole by $Fe^{III}(acac)_3$ *and Hydrogen Peroxide.*—The deuterium content of the 4-methoxyphenol from the oxidation of 4-deuterioanisole with $Fe^{III}(acac)_3$ and hydrogen peroxide gave a value of 9.4% for the NIH shift.[11]

The Dissolution of Potassium Hexacyanoferrate(II) *and Hexacyanoferrate*(III) *in Benzene by the Use of the Phase-transfer Agent, Adogen 464, and the Attempted Oxidation of these Benzene Solutions with Hydrogen Peroxide.*—There is no measurable extraction of potassium hexacyanoferrate(III) from aqueous solution when shaken with benzene. However, in the presence of Adogen 464 (a methyltrialkylammonium chloride phase-transfer agent) there is a rapid uptake of the hexacyanoferrate(III) anion into the organic phase. By the use of u.v.–visible spectrophotometry it is possible to measure the partitioning of the hexacyanoferrate(III) anion between the two phases as a function of the Adogen 464 concentration. Table 4 shows that with an Adogen : anion molar ratio of *ca.* 3 : 1 all the hexacyanoferrate(III) anion is extracted from the aqueous solution. Similarly, for potassium hexacyanoferrate(II) *ca.* 4 mol. equiv. of the Adogen are needed for complete extraction of the hexacyanoferrate(II) anion from water (Table 5). Adogen 464 will solubilise these anions in other aromatic compounds, for example anisole and chlorobenzene, and other organic solvents, such as tetrachloromethane, trichloromethane, and dichloromethane, but not in hexane. Attempts to dissolve the two anions directly in benzene in the presence of Adogen 464 were unsuccessful.

When hydrogen peroxide was added to a solution of Adogen 464 and hexacyanoferrate(II) anion in benzene the initially colourless solution was oxidised to the yellow hexacyanoferrate(III) anion. However, h.p.l.c. and g.l.c. analysis of the solution failed to detect phenol. Likewise, no phenol was detected when benzene solutions containing equimolar quantities of hexacyanoferrate-(II) and -(III) anions were treated with hydrogen peroxide, even after the mixture had been heated to reflux. Substitution of the benzene by chlorobenzene or anisole similarly gave no phenolic products. No reaction with the benzene occurred when the hydrogen peroxide was replaced by iodosylbenzene, t-butyl hydroperoxide, cumene hydroperoxide, or sodium iodate(VII). The analytical method would have been able to detect phenol yields greater than 0.4%, based on hydrogen peroxide added. H.p.l.c. analysis showed that phenol, equivalent to the amount of hydrogen peroxide used above, in benzene containing Adogen 464 and both hexacyanoferrate anions is not consumed following the addition of hydrogen peroxide. Similarly, chlorophenols in chlorobenzene and methoxyphenols in anisole are not oxidised by hydrogen peroxide in the presence of hexacyanoferrate anions.

TABLE 3

Yield of products from the oxidation of toluene and anisole by $Fe^{III}(acac)_3$ and hydrogen peroxide

Substrate	Reaction conditions	Yield of products * (%) PhCHO	$PhCH_2OH$	PhOH	ArOH	Isomer distribution of substituted phenols (%) 2	3	4
Toluene	N_2	2.0	1.7		1.6	52	21	28
Anisole	Air			2.4	3.4	87	1	12

* Product yields determined by g.l.c. analysis and based on H_2O_2.

TABLE 4

Partitioning of hexacyanoferrate(III) anion between equal volumes of water and benzene in the presence of Adogen 464: total concentration of $Fe(CN)_6^{3-}$, 0.5 mM

Molar ratio					
Adogen : hexacyano-ferrate(III)	0	0.95	1.89	2.86	3.50
Hexacyanoferrate(III) in benzene (%)	0	29.8	57.1	85.6	100
Hexacyanoferrate(III) in water (%)	100	70.2	42·9	15.4	0

TABLE 5

Partitioning of hexacyanoferrate(II) anion between equal volumes of water and benzene in the presence of Adogen 464: total concentration of $Fe(CN)_6^{4-}$, 0.5 mM

Molar ratio						
Adogen : hexacyano-ferrate(II)	0	0.82	1.64	2.48	3.29	4.13
Hexacyanoferrate(II) in benzene(%)	0	30.6	47.5	67.5	83.7	95.6
Hexacyanoferrate (II) in water (%)	100	69.4	52.5	32.5	16.3	4.4

DISCUSSION

Previous to this study it was not known whether hydrogen peroxide with iron compounds dissolved in benzene or benzene derivatives would bring about aromatic hydroxylation and what effect changing the reaction medium from water to an essentially non-polar aromatic solvent would have on the nature of the attacking species. Indeed, apart from some recent reports by Tezuka and his co-workers [12] on aromatic hydroxylation by hydroxyl radicals generated by photolysis or thermolysis of α-azohydroperoxides dissolved in aromatic compounds, little is known of the reactions of the hydroxyl radical in a non-aqueous medium.

The results from this study show that the addition of hydrogen peroxide to a benzene solution of $Fe^{III}(acac)_3$ in air gives phenol whilst under anaerobic conditions the reaction produces phenol and biphenyl. The analogous reactions with Fenton's reagent and an aqueous suspension of benzene give closely similar results.[2a]

The data from extensive studies with Fenton's reagent are consistent with the attacking species in an aqueous medium being the hydroxyl radical derived from the iron(II)-catalysed decomposition of hydrogen peroxide [reactions (1)—(5)].[13] This radical reacts with benzene by addition to give hydroxycyclohexadienyl radicals

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \qquad (1)$$

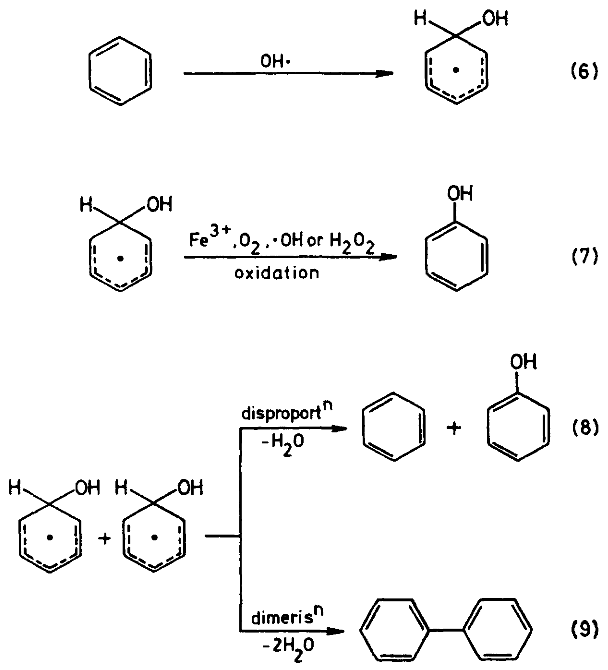
$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + {}^{\bullet}O_2H + H^+ \qquad (2)$$

$$Fe^{2+} + {}^{\bullet}OH \longrightarrow Fe^{3+} + OH^- \qquad (3)$$

$$Fe^{3+} + {}^{\bullet}O_2H \longrightarrow Fe^{2+} + O_2 + H^+ \qquad (4)$$

$${}^{\bullet}OH + H_2O_2 \longrightarrow OH^- + {}^{\bullet}O_2H + H^+ \qquad (5)$$

which by subsequent oxidation or disproportionation or dimerisation and dehydration lead to phenol or biphenyl, respectively [reactions (6)—(9)]. It seems likely that the attacking species derived from hydrogen peroxide and $Fe^{III}(acac)_3$ in benzene is also the hydroxyl radical which produces phenol and biphenyl in an analogous manner to Fenton's reagent in aqueous solution. This conclusion is reinforced by the oxidation of anhydrous benzene by the photolysis or thermolysis of α-azohydroperoxides which also give phenol as the sole product in air and phenol and biphenyl under argon.[12a]



Since, however, the hydrogen peroxide used in this study is an aqueous peroxide mixture (78% H_2O_2) it is possible that the observed oxidation might be occurring in an aqueous or aqueous hydrogen peroxide suspension or layer on the surface of the reaction vessel. Indeed, a close examination of the reaction mixtures revealed that the benzene contained a fine suspension, presumably of undissolved aqueous hydrogen peroxide. We investigated this possibility in three ways. First, we examined the effect of adding a cosolvent to the reaction mixture that would solubilise the water and hydrogen peroxide. When the oxidation of benzene was carried out in the presence of increasing proportions of acetonitrile there was no marked change in the product distribution other than a reduction in yield associated with the dilution of the substrate benzene. Secondly, the oxidations were carried out using solutions of hydrogen peroxide in benzene to which were added the $Fe^{III}(acac)_3$ and these experiments gave comparable results to the reactions where the hydrogen peroxide was added to the $Fe^{III}(acac)_3$ in benzene. In the third set of experiments the somewhat polar glass surface of the reaction vessel was replaced by hydrophobic polythene; however, this had no effect on the yield or distribution of products. Thus we conclude that whether the reaction mixture is heterogeneous or homogeneous the same oxidation mechanisms occur.

The reaction of hydrogen peroxide with a toluene solution of $Fe^{III}(acac)_3$ under nitrogen gives products from nuclear and side-chain oxidation. The presence of bibenzyl is indicative of the participation of benzyl radicals formed directly by hydrogen-atom abstraction or indirectly by the addition of the hydroxyl radical to toluene followed by dehydration of the methylhydroxycyclohexadienyl radical.[9] The benzyl radicals are also precursors of the other side-chain oxidation products, benzyl alcohol and benzaldehyde.

The relative proportions of nuclear to side-chain attack in the reaction of hydroxyl radicals with toluene in aqueous medium is known to be dependent on the reaction conditions. Thus good oxidants favour oxidation of the methylhydroxycyclohexadienyl radicals over their dehydration to benzyl radicals with a consequent decrease in side-chain oxidation, whilst increased acidity leads to a preference for dehydration.[2b,4d,9] Similarly the cresol isomer distribution is markedly dependent on the oxidation conditions.[4d,9] The product distribution obtained in this study is typical of those obtained from the oxidation of toluene by the hydroxyl radical in an aqueous medium [2,4d,9] and is similar to that obtained from the hydroxyl radical in anhydrous toluene.[12b]

The oxidation of anisole with hydrogen peroxide and $Fe^{III}(acac)_3$ gives the three methoxyphenols and phenol. The distribution of the methoxyphenols obtained in this study is closely similar to the values obtained for anisole with Fenton's reagent in aqueous solution [2b] and from hydroxylation with hydroxyl radicals from the photolysis of α-azohydroperoxides.[12] However, it is noteworthy that, as is found with toluene, the phenolic isomer distribution for the hydroxylation of anisole by the hydroxyl radical is sensitive to the reaction conditions.[2b,4e] The low value of the NIH shift from the hydroxylation of 4-deuterioanisole is consistent with the active species being the hydroxyl radical and the oxidation involving radical rather than cation intermediates.[1,14]

From the work of Groves and his co-workers [15] and Yamamoto and Kimura [16] on the hydroxylation of alkanes and epoxidation of alkenes with iron compounds and hydrogen peroxide, alkyl peroxides, and iodosylbenzene in non-aqueous media, and from recent work on oxidations mediated by these oxidants and cytochrome P-450,[17] an alternative active species to the hydroxyl radical is the ferryl ion, $Fe^{IV}O$. This species might be formed by the heterolysis of the hydrogen peroxide [reaction (10)].[18] Such an oxidant could give

$$Fe^{II} + H_2O_2 \xrightarrow{H^+} Fe^{IV}O + H_2O \qquad (10)$$

phenol by insertion into the aromatic C=C bonds followed by rearrangement of the arene oxide (with a concomitant large value of the NIH shift), insertion into the C–H bonds or, acting as a radical, by addition to the aromatic ring. However, the similarities of the results from this study with those from aromatic hydroxylation by the hydroxyl radical in aqueous media and with those from the photolysis of α-azohydroperoxides in anhydrous conditions in the absence of metal compounds leads us to conclude that the hydroxyl radical is the common active species. When the hydrogen peroxide in these oxidations was replaced by iodosylbenzene with either $Fe^{III}(acac)_3$ or with Fe^{III}TPPCl there was no oxidation of benzene. Two other oxidants, namely t-butyl hydroperoxide and cumene hydroperoxide (which promote oxidation in the presence of cytochrome P450), were also unreactive towards $Fe^{III}(acac)_3$ in benzene.

The poor conversion of the hydrogen peroxide into aromatic oxidation products in the reaction of hydrogen peroxide with solutions of $Fe^{III}(acac)_3$ in aromatic compounds was unexpected. It was hoped that by having the aromatic compound as substrate and solvent it would be present in sufficiently large excess to trap effectively all the hydroxyl radicals generated from the hydrogen peroxide. In an aqueous medium with a low concentration of the aromatic compounds the hydroxyl radical is competitively removed by reaction with iron(II) [reaction (3)] and phenolic products. The low yield was shown not to be due to the loss or further reaction of the phenolic products. Thus the yield of phenol from the oxidation of benzene remained unchanged when the reaction was analysed 24 h after the addition of the hydrogen peroxide instead of the normal 1—1.5 h and a mixture of phenol in benzene, at a concentration typical of that formed in a product mixture, when treated with hydrogen peroxide and $Fe^{III}(acac)_3$ showed no evidence of further oxidation of the phenol. The low yields did not arise from the slow or incomplete reaction of the hydrogen peroxide since when more hydrogen peroxide was added to a reaction of benzene, which g.l.c. analysis showed to have stopped, the phenol yield increased. Repeated additions of hydrogen peroxide consistently gave the same yield of oxidation products per portion of oxidant. It seems most likely that the low yield of aromatic oxidation products is due to the reaction of the hydroxyl radicals with the acetylacetone ligand in the acetylacetonatoiron complex. Thus although the overall concentration of benzene is much greater than the acetylacetone, the local concentration of the ligand at the site of generation of the hydroxyl radical on the iron and the probable comparable reactivity of acetylacetone and benzene are sufficient to ensure that the acetylacetone is attacked preferentially and that the yields of aromatic oxidation products are small. In agreement with this conclusion it is possible that the iron-containing deposits obtained during the course of these oxidations arise from the oxidation of acetylacetone.

In an attempt to overcome the problem of ligand oxidation we examined oxidations with several other benzene-soluble iron complexes. $Fe^{II}(acac)_2$ not unexpectedly behaved like the iron(III) complex; however, iron(III) chloride gave no oxidation of benzene. Fe^{III}TPPCl, ferrocene, and pentacarbonyliron reacted more slowly than $Fe^{III}(acac)_3$ and only $Fe^{III}TPPCl$ gave comparable yields of phenol. The absence of biphenyl in the reactions of the last three iron compounds under nitrogen may result from the slowness of these oxidations. A decrease in the rate of production of hydroxyl radicals and hence of hydroxycyclohexadienyl radicals would disfavour the formation of biphenyl [reaction (9)] which is dependent on the square of the concentration of the adduct radicals. A similar dependence of biphenyl formation on the rate of production of hydroxyl radicals has been observed in the oxidation of aqueous suspensions of benzene with Fenton's reagent.[2a]

Recently there have been several reports of the solubilisation of inorganic oxidants in organic solvents by the use of phase-transfer reagents. Thus benzene solutions of manganate(VII) ion [19] and dichromate(VI) ion,[20] with tetra-alkylammonium ions as the phase-transfer cations, have been prepared and used as oxidants in organic chemistry. In this study we have shown that the tetra-alkylammonium chloride, Adogen 464, is an effective phase-transfer agent for the solubilisation of both hexacyanoferrate anions in benzene. A brief study of the stoicheiometry of the phase-transfer process revealed that the hexacyanoferrate(III) and hexacyanoferrate(II) anions require the expected 3 and 4 mol. equiv. of Adogen 464, respectively, for complete solubilisation.

It was hoped that the hexacyanoferrate(II) anion which we have found can promote the hydroxylation of benzene and benzenoid compounds in aqueous solution [21] would bring about the same reaction when solubilised into benzene. However, despite the oxidation of the benzene-solubilised hexacyanoferrate(II) to hexacyanoferrate(III) by hydrogen peroxide no phenol was detected. We attribute the failure to hydroxylate aromatic compounds not to the lack of formation of hydroxyl radicals but to the reaction of this radical with the phase-transfer agent. The immediate environment of the hydroxyl radical when generated in the aromatic solvent will be the extensive hydrocarbon chains of the phase-transfer agent and not the aromatic compound. Consequently it is the alkyl chains that are attacked in preference to the aromatic compound.

The work described in this paper represents the first solubilisation of hexacyanoferrate-(II) and -(III) anions in a non-polar organic solvent. Despite the failure to bring about aromatic hydroxylation with these anions and hydrogen peroxide it is probable that an organic solution of the ubiquitous oxidant hexacyanoferrate(III) may well find other uses in organic chemistry.

EXPERIMENTAL

Materials.—All the materials were commercial reagent grade unless otherwise stated and were obtained from Aldrich Chemical Co. Ltd., Koch-Light Ltd., or Fisons Scientific Apparatus Ltd. The nitrogen gas (British Oxygen white spot) was dried by passing it through concentrated sulphuric acid followed by silica gel and potassium hydroxide pellets. t-Butyl hydroperoxide (Aldrich Chemical Co. Ltd.) was a 70% solution in water. Adogen 464 was from Aldrich Chemical Co. Ltd. The hydrogen peroxide (78% in water) was obtained from Interox Chemicals Ltd. The aromatic substrates were all purified by distillation prior to use. [4-^{2}H]Anisole contained 78.9% deuterium and was prepared from 4-bromoanisole as described previously.[2b] Iodosylbenzene was prepared and its active oxygen content determined following Saltzman and Sharefkin.[22] Tetraphenylporphinatoiron(III) chloride was prepared following Rothemund and Menotti.[23]

Methods.—Glass columns were used in a Pye-Unicam GCD gas chromatograph with a flame ionisation detector for g.l.c. analyses. The packing materials for these analyses have been described previously.[24] For combined g.l.c.–mass spectrometry a Pye 104 gas chromatograph was coupled to an AEI MS 30 spectrometer. H.p.l.c. analyses were carried out with a Du Pont 830 chromatograph using stainless steel columns (25 × 0.4 cm) packed with Partisil-10 ODS (Whatman) coupled to a Du Pont 837 variable wavelength u.v. detector.

U.v. and visible spectra were recorded on a Pye-Unicam SP 800 or SP 8 000 spectrophotometer.

Oxidations using $Fe^{III}(acac)_3$ *and Hydrogen Peroxide.*—The standard procedure was as follows. Hydrogen peroxide (0.14 mmol) was added to a solution of $Fe^{III}(acac)_3$ (0.1 mmol) in the aromatic compound (2 cm^3), the mixture was sealed with a Subaseal (Fisons Scientific Apparatus Ltd.) and mechanically shaken during the course of the reaction. For reactions in the absence of air the solution of $Fe^{III}(acac)_3$ was flushed with dry nitrogen for *ca.* 1 min prior to the addition of the hydrogen peroxide. The reactions were monitored by removing samples with a syringe for g.l.c. analysis.

For reactions with repeated additions of hydrogen peroxide, the standard procedure was modified by adding the hydrogen peroxide in four separate portions (each 0.14 mmol). Portions 2—4 were added when g.l.c. analysis showed that the oxidation from the previous portion of hydrogen peroxide was complete.

Other modifications of the procedure involved omitting or reducing the concentration of $Fe^{III}(acac)_3$, omitting the hydrogen peroxide, and replacing the glass reaction flask with a polythene container.

Oxidation of Benzene using a Solution of Hydrogen Peroxide in Benzene.—Benzene (100 cm^3) was shaken with hydrogen peroxide (2 cm^3) for 2 h and allowed to stand. The $Fe^{III}(acac)_3$ (0.1 mmol) was dissolved in a portion (2 cm^3) of the benzene solution of hydrogen peroxide and the mixture was shaken and analysed as described above.

Oxidation of Benzene with $Fe^{III}(acac)_3$ *and Hydrogen Peroxide in the Presence of Acetonitrile.*—The procedure used for these oxidations was the same as the standard procedure described above for reactions under nitrogen except that the benzene was replaced by mixtures of benzene and acetonitrile (total volume 2 cm^3).

NIH Shift Experiments.—Hydrogen peroxide (10 portions of 0.07 mmol) was added to $Fe^{III}(acac)_3$ dissolved in [4-^{2}H]anisole (1 cm^3) and the mixture was shaken in air. The deuterium content of the 4-methoxyphenol was determined by combined g.l.c.–mass spectrometry.

Determination of Iron Content of Dark Deposit in Oxidations with $Fe^{III}(acac)_3$ *and Hydrogen Peroxide.*—Hydrogen peroxide (20 portions of 0.5 cm^3) was added to $Fe^{III}(acac)_3$ (5 mmol) in benzene (100 cm^3). The almost black lower layer in the mixture was removed, shaken with ether, separated, and evaporated to dryness. The solid was refluxed with concentrated HCl for 2 h and a mixture of concentrated HCl and concentrated HNO_3 for 4 h to give a solution of iron(III) ions. The iron(III) was determined colorimetrically by complex formation with potassium thiocyanate.[25]

Oxidation of Benzene with Hydrogen Peroxide and a Selection of Iron Compounds.—The standard procedure was modified by replacing the $Fe^{III}(acac)_3$ with an equivalent amount of one of the following: $Fe^{II}(acac)_2$, Fe^{III}TPPCl, ferrocene, pentacarbonyliron, or iron(III) chloride.

Attempted Oxidation of Benzene with $Fe^{III}(acac)_3$ *or* Fe^{III}TPPCl *and a Selection of Oxidants.*—One of the following oxidants, iodosylbenzene (saturated, the mixture contained solid iodosylbenzene since the oxidant is not very soluble in benzene), or cumene hydroperoxide, or t-butyl hydroperoxide (0.075 mmol), was used in place of hydrogen peroxide in the standard procedure. The attempted reaction with iodosylbenzene was also repeated using Fe^{III}TPPCl in place of $Fe^{III}(acac)_3$.

The Dissolution of Hexacyanoferrate(II) *and Hexacyanoferrate*(III) *Ions in Organic Solvents.*—A 1mM aqueous solution (50 cm^3) of potassium hexacyanoferrate(III) was shaken with benzene (50 cm^3) in the presence of increasing quantities of Adogen 464. The concentration of oxidant in each layer was determined spectrophotometrically by monitoring the absorption of the aqueous hexacyanoferrate(III) anion at 418 nm (420 nm in benzene). This experiment was repeated using anisole, chlorobenzene, dichloromethane, chloroform, or hexane in place of benzene.

The solubilisation of the hexacyanoferrate(II) anion in benzene was studied in the same way monitoring absorption at 325 nm.

Attempted Oxidation with Hydrogen Peroxide and Hexacyanoferrate Anions and Adogen 464.—To a freshly prepared 1 or 10mM solution of hexacyanoferrate(II) solubilised in benzene, anisole, or chlorobenzene using Adogen 464, was added an equivalent amount of hydrogen peroxide. The mixture was monitored by g.l.c. and h.p.l.c. over 10 h.

The attempted oxidation was repeated using an equimolar solution of both hexacyanoferrate anions in benzene and heating the mixture to reflux.

In other attempted oxidations of benzene, the hydrogen peroxide was replaced by iodosylbenzene, cumene hydroperoxide, t-butyl hydroperoxide, or sodium iodate(VII).

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